Treatability of five micro-pollutants using modified Fenton reaction catalysed by zero-valent iron powder (Fe(0))

Goswami, Anuradha; Jiang, Jia-Qian; Petri, Michael

Published in:
Journal of Environmental Chemical Engineering

DOI:
10.1016/j.jece.2021.105393

Publication date:
2021

Document Version
Publisher's PDF, also known as Version of record

Journal of Environmental Chemical Engineering 9 (2021) 105393

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Treatability of five micro-pollutants using modified Fenton reaction catalysed by zero-valent iron powder (Fe(0))

Anuradha Goswami [a], Jia-Qian Jiang [a,*,1], Michael Petri [b]

[a] Department of Civil Engineering and Environmental Management, Glasgow Caledonian University, Glasgow G4 0BA, Scotland, UK
[b] Lake Constance Water Supply, Germany

ARTICLE INFO

Editor: Teik Thye Lim

Keywords:
Adsorption
Advanced oxidation processes
BMG model
Degradation
Emerging micro-pollutants
Fe(0)-catalytic Fenton oxidation
Mineralisation
Water treatment

ABSTRACT

Diuron, gabapentin, sulfamethoxazole, terbutryn and terbuthylazine are emerging micro-pollutants with concentrations in water and wastewater ranging from tens of ng/L to >10 μg/L levels. The Fenton oxidation catalysed either by zero-valent iron (Fe(0)) or by Fe(II) salts was studied to treat the targeted micro-pollutants and their mixtures at compound concentrations between 1 and 1000 μg/L. The Fe(0)-catalytic Fenton oxidation exhibited complete degradation of all micro-pollutants at initial solution pH 3 but at pH 5, the degradation was 90% for diuron, 80% for gabapentin, 95% for sulfamethoxazole, 100% for terbutryn and 70% for terbuthylazine, respectively. Moreover, dissolved organic carbon in multiple micro-pollutant solutions can be reduced by 70% at pH 3 and 46% at pH 5, which were much better than Fe(II)-catalytic Fenton reaction for the same pH conditions. SEM/EDX analysis showed the corrosion of iron surface and FTIR analysis evidenced the adsorption of oxidation by-products onto solid iron surface. Additionally, the toxicity of effluent after the treatment was reduced to minimal and the Behnajady-Modirshahla-Ghanbery (BMG) model fitted well to the kinetics of the mineralisation of the studied micropollutants. Finally, Fe(0) catalyst can be reused up to three times and the process produced no or less sludge at pH 3 and pH 5, respectively. The impact of this study is that the Fe(0)-catalytic Fenton oxidation would be an alternative to the traditional Fenton reaction to combat the environmental issues caused by the emerging micro-pollutants.

1. Introduction

Rapid increase in recalcitrant contaminants in the environment and the associated adverse effects on human health and ecosystem have been observed due to extensive use of chemicals globally [1–4]. These pollutants can be physical, chemical, or biological species which raise the aesthetic or detrimental hazard on aquatic ecosystems. Large sized particles causing water disharmony are easy to treat. However, a rising concern is the existence of micro-pollutants, which are usually found in concentration levels of ng/L to μg/L and deteriorate the water quality henceforth, posing a threat to the ecosystems [3].

Due to continuous discharge of pharmaceuticals, steroids, pesticides, and many more synthetic chemicals, micro-pollutants are widely distributed in the environment. Some of these compounds are recalcitrant hence, difficult to treat. Therefore, they persist in the environment due to extended half-life [5]. Several researchers have detected high levels (> 10 μg/L) of pharmaceuticals, precisely paracetamol, gabapentin, codeine, tramadol, and atenolol detected in raw wastewaters [6]. Among all studied compounds, gabapentin did not degrade into its metabolite, and thus, 100% of the gabapentin dispensed were detected [7]. Pesticides/biocides are generally toxic and resistance to biological treatment. These compounds are also commonly drained through soils and leached into the groundwater [8]. And therefore, they tend to accumulate in the environment causing long-term pollution.

Diuron has been the most frequently detected pesticide in water [9, 10] and its elevated contents pose a hazard to aquatic life and can have human health implications [11]. Gabapentin has been classified as the drug in Class C controlled substance [12] and evolved as an emerging micro-pollutant. Sulfamethoxazole is an antibiotic and sparingly soluble in water. With its low KOC value, sulfamethoxazole is conducive for leaching potential [13] and its residuals in water pose a threat to human health and the ecosystem [14]. Terbutryn and terbuthylazine are selective herbicides that belong to the triazines type compounds, which are usually toxic and tend to accumulate in the environment causing

* Corresponding author.
E-mail address: jiaqian.jiang@gcu.ac.uk (J.-Q. Jiang).
[1] ORCID: https://orcid.org/0000-0003-3607–8910.

https://doi.org/10.1016/j.jece.2021.105393
Received 5 January 2021; Received in revised form 16 March 2021; Accepted 19 March 2021
Available online 26 March 2021

prolonged pollution [8,15]. The stated five organic compounds were chosen for this study based on the occurrence of each micro-pollutant in water and wastewaters (Table 1) and these compounds are placed in the Watch List given by the European Union Water Framework Policy and Annex III inventory [16].

The growth of water and environmental pollution has called for an ultimate demand to develop viable technologies to combat the resistant chemical contaminants. Ozonation is among the widely studied and practised oxidation technology, which can achieve high efficiency to degrade numerous pollutants; however, it does not mineralise the compounds so efficiently [23]. As an outcome, the by-products formed after the oxidation can be toxic in water bodies [24].

Advanced Oxidation Processes (AOPs) have been practised at laboratories to oxidise and mineralise recalcitrant contaminants [25,26] and reduce the wastewater toxicity [27,28]. Table 2 provides examples of the targeted micro-pollutants' treatability by various AOPs. In general, UV irradiation induced photocatalytic oxidation is one of the most common AOPs where either ozone or peroxide or Fenton reagent is widely used as the oxidant and TiO_2 or metal oxide as the catalyst. Boron-doped TiO_2 was more active than bare TiO_2 in performing the catalysis [29] and combined application of UV/H_2O_2 had high treatment efficiency in comparison with O_3/H_2O_2 or ozone alone in the wastewater tertiary treatment [30].

The Fenton oxidation was initially driven by the oxidation of tartaric acid with hydrogen peroxide catalysed by ferrous ions in 1894 [36] and since then, it has been researched for the non-selective degradation of recalcitrant organic substances, accompanying by the exploration of reaction mechanisms, studying on the sludge development and toxicity assessment after the Fenton oxidation [37–42]. The Fenton oxidation reaction is classified as either homogenous or heterogeneous status, based on the catalyst (iron) sources. In a homogeneous status, ferrous iron salts act as catalyst, and ferric-hydroxide sludge is accumulated at pH 4 or higher, which affects the oxidation competence [43]. The process is limited to use at a large-scale application due to many factors like consumption of catalyst, high sludge production and the requirement of low operating pH (most cases at pH 3) to initiate the process [3]. The major issues retained with the classical Fenton oxidation is the operational cost from heavy sludge production and the pH adjustment and neutralisation of effluent after the treatment. These drawbacks limit the usage of the classical Fenton oxidation at industrial scale [44]. On the other hand, heterogeneous Fenton oxidation uses solid irons including zero-valent iron Fe(0) powder as catalyst, which are oxidised to soluble Fe (II)/(III) ions to progress the Fenton reactions. Compared with ferrous iron as catalyst, solid iron could be beneficial in surface reactivity and reduction of iron sludge production; and then it could broaden the scope of Fe(0) powder application as an alternative catalyst to the Fe(II) ion for the Fenton oxidation.

In terms of the literature review, the advantages of Fe(0) catalytic Fenton oxidation have not been fully explored and then we hypothesize innovative components of the process as 1) synergistic functions of catalysis and adsorption of Fe(0) powder in the Fenton reaction, 2) much less sludge production will be achieved due to the property of the Fe(0) powder, and 3) acceptable reusable performance of Fe(0) catalyst.

Table 1
Occurrence of five micro-pollutants in water and wastewater.

Analyte/classification	Occurrence	Source	Ref.
Diuron/ pesticide	26.6 ng/L	Groundwater	[17]
	500 ng/L	River Ebro	[8]
Gabapentin/epileptic drug	1285 ng/L	Wastewater	[18]
	13.2 ± 3.3 μg/L	Raw wastewater	[19]
Sulfamethoxazole/antibiotics	21 ng/L	Groundwater	[20]
Terbutryn/pesticide (Triazine class)	5600 ng/L	Surface water	[21]
Terbuthylazine/ pesticide (Triazine class)	>100 ng/L	Groundwater	[22]

Table 2
Examples of the treatability of the targeted micro-pollutants (MP) by Advanced Oxidation Processes (AOPs).

MP	AOP	Remark	Ref.
Diuron (Aqueous solution)	Platinized (Pt) TiO_2 (Photocatalytic ozonation)	Degraded after 20 min treatment. 97% diuron mineralised under UV irradiation after 8 h of treatment. Pt-TiO_2 was catalysed four times higher than P-25 TiO_2.	[31]
Gabapentin (Wastewater effluent)	Photocatalytic oxidation (P-25 TiO_2 or ZnO/UV)	ZnO catalytic UV irradiation: 40 min sufficient for 95% degradation. The reaction rate for ZnO was six times faster than P-25 TiO_2.	[32]
Sulfamethoxazole (Wastewater)	Ultrasonic/O_3 oxidation	The toxicity of the solution was faded, and biodegradability increases from 0 to 0.54.	[33]
Terbutryn (Well water)	Solar photodegradation; Photocatalytic degradation (TiO_2/H_2O_2, Fe^{3+}/H_2O_2, TiO_2/Fe^{3+}/H_2O_2)	$TiO_2/Fe^{3+}/H_2O_2$ achieved the max. degradation at 3.5 h in natural sunlight; longer exposure was required for more/ complete detoxification. Long-chain fatty acid derivatives and phthalates esters were quite resistant to all treatments practised.	[34]
Terbuthylazine (Aqueous solution)	UV_{254} photolysis, UV_{254}/H_2O_2; Single Ozonation; O_3/H_2O_2; Catalytic ozonation (e.g., MWCNT, TiO_2 as a catalyst); TiO_2 photocatalytic oxidation	UV_{254}/H_2O_2- best removal of terbuthylazine; Catalytic ozonation-enhance O_3 performance; the degradation mechanism of terbuthylazine via either O_3 molecule or free radical $^{\bullet}OH$	[15]
SMX, GBP, DIU, TBR (municipal wastewater effluent)[a]	UV_{254} alone; Fenton ($Fe^{2+,\ 3+}/H_2O_2$); Photo-Fenton ($Fe^{2+,3+}/H_2O_2$/ with light)	~Neutral pH condition. Photo-Fenton (UV_{254})- 97% of the pollutants were removed after 30 min (H_2O_2 50 mg/L, Fe^{2+} 5 mg/L). The process of UV_{254} alone, Fenton or Photo-Fenton under sunlight showed poor % removal.	[35]

[a] SMX, sulfamethoxazole; GBP, gabapentin; DIU, diuron; TBR, terbutryn; TBZ, terbuthylazine.

Confirmation of these hypothesises will contribute to elucidate the superior performance of Fe(0) catalytic Fenton oxidation and then to propose the possibility of the technology applied in practical water and wastewater treatment. Thus, this research aims to explore the role and mechanisms of Fe(0) powder in the Fenton reaction and to rationalise if the Fe(0) catalyst could be used to perform the large scale Fenton reaction.

To achieve the stated aims of the study, the performance of Fe(0)-catalytic and Fe(II)-catalytic Fenton oxidations were compared. As mentioned early, that the studied micropollutants were pharmaceuticals (sulfamethoxazole, gabapentin) and pesticides (diuron, terbutryn, terbuthylazine). The concentrations of the target micro-pollutants in water and wastewater ranged from tens of ng/L to >10 μg/L levels (Table 2)

and then we chose the range of between 1 and 1000 μg/L to study the comparative performance of Fe(0)/Fe(II) catalytic Fenton processes by analysing the degradation of micro-pollutants, toxicity reduction, sludge production and mineralization efficiency. The potential of Fe (0)-catalytic Fenton oxidation was also assayed from mineralisation kinetics of the micro-pollutants. The mechanism of the developed method was examined for the event of adsorption and oxidation effects during the treatment. Also the treatment sustainability and possible degenerative by-products adhering onto the corroded iron surface during the treatment were investigated.

2. Materials and methods

2.1. Materials

Five micro-pollutants, namely diuron, gabapentin, sulfamethoxazole, terbutryn and terbuthylazine, were studied for their removal by both the heterogeneous Fe(0) catalytic- and traditional homogeneous Fe (II) catalytic-Fenton oxidation processes. The chemicals used in the study are given in Table 3.

Fresh Fe(0) powder was purchased from Sigma Aldrich (item code 12310) with Fe content of ≥99% and the density of 7.86 g/mL. Specific surface area (as surface area/volume) of 0.38 μm^{-1} was gained by the calculation from three consecutive slices in the SEM image with standard deviation ranging from 0.03 to 0.11 μm^{-1} (Supplementary material - Image J software: area thresholding method). The fresh Fe(0) powder was stored in dark plastic bottle at room temperature and stable in the absence of water exposure and under ambient condition.

2.2. Characterization of Fe(0) catalyst

Scanning electronic microscopy (SEM)/energy-dispersive X-ray spectroscopy (EDX) analysis was performed by the Carl Zeiss EVO 50 microscope with AztecEnergy acquisition software (Oxford Instruments) and XmaxNand X-act silicon drift detector. The SEM micrograph was taken at 100 μm resolution and 1000x magnification. SEM was run in high vacuum mode with accelerating voltage of 15 kV and working distance (WD) of 9 mm. Chemical characterisation of Fe (0) catalyst by quantitatively elemental composition analysis was obtained from X-ray mapping data using SEM-linked to EDX.

The structure of organic-Fe complexes adsorbed onto the iron powders' surface was examined by the standard FTIR procedure (JASCO FT/IR-6100). The obtained IR spectrum was normalised and examined by Bio-Rad software (KnowItAll® Informatics System, ID Expert Bio-Rad Laboratories). The surface area of Fe powder was estimated from the SEM micrograph by Image J. software using the area thresholding method.

Table 3
List of chemicals used and test purpose.

Chemicals	Usage	Supplier
2.5 L Methanol, for HPLC	LC-MS/MS gradient	Fisher Scientific
Deferoxamine mesylate salt	H_2O_2 quencher	Sigma Aldrich
Diuron	Analyte studied	Sigma Aldrich
Fe powder(fine) [Item Code 12310]	Fenton Oxidation experiment	Sigma Aldrich
Ferrous Ammonium Sulfate Heptahydrate, 98.5–100%, (ACS Reagent Grade)	Fenton Oxidation experiments	Fisher Scientific
Gabapentin	Analyte studied	Sigma Aldrich
Hydrochloric Acid, 37%, Certified AR for Analysis, d = 1.18	DOC analysis	Fisher Scientific
Hydrogen peroxide, for analysis, 35 wt% solution in water, stabilised, ACROS Organics™	Oxidant used in experiments	Fisher Scientific
Iron(II) sulfate heptahydrate, 99.5%, for analysis, ACROS Organics™	Fenton Oxidation experiments	Fisher Scientific
Lumi Multi-Shot bacteria	Toxicity analysis	ENVITECH Ltd
Potassium Permanganate, Certified AR	Fe^{2+} analysis	Fisher Scientific
Sodium hydroxide pellets	Adjusted pH	Fisher Scientific
Sodium thiosulphate	Fenton oxidation quencher	Fisher Scientific
Sulfamethoxazole	Analyte studied	Sigma Aldrich
Sulfuric Acid Min 95% d = 1.83, Certified AR,	Adjusted pH	Fisher Scientific
Terbuthylazine	Analyte studied	Sigma Aldrich
Terbutryn	Analyte studied	Sigma Aldrich

2.3. Experimental procedures and reaction kinetics

The test solutions containing micro-pollutants were prepared in tap water. The stock solutions and the micro-pollutants working solution for the kinetic study were prepared in distilled water generated by PURELAB ® Classic ELGA 26600. The pH of the solution was adjusted with 0.1 M or 1 M NaOH and 0.1 M or 1 M H_2SO_4. The detailed information on the preparation of working solutions is given in Fig. S1.1. The tap water quality was obtained from the Scottish water annual report [45].

The Fenton oxidation batch experiments were conducted by Kemira flocculator (Flocculator 2000, Kemira, Helsingborg, Sweden). All experiments were conducted at ambient room temperature and atmospheric pressure in one-litre glass beakers. The test solutions were mixed at 400 rpm for one minute, 80 rpm for adequate reaction time, and then remained undisturbed for 30 min to deploy the sedimentation. The Taguchi Method (Table S1.1) was used to obtain the operating conditions of the Fe(0)- and/or Fe(II) catalytic Fenton oxidations. Experimental factors such as initial solution pH, ratios of H_2O_2:Fe(II)/Fe(0) and reaction time of each parent compound (diuron, gabapentin, sulfamethoxazole, terbutryn and terbuthylazine) and their mixture solution ($M^P{}_m$) were optimised, which are given in Tables S1.2 and S1.3. The effluents obtained were filtered from 0.45 μm nylon filter in vacuum filtration for DOC analysis and filtered with a 0.2 μm nylon syringe filter for the analysis of micro-pollutants concentration.

The kinetic studies were conducted using each test solution with micro-pollutant concentration of 100 μg/L and Fe(0) catalytic Fenton reaction at pH 5. The first- and second-order and BMG kinetic models [46] were applied to derive the rate constants for the mineralisation of diuron, gabapentin, sulfamethoxazole, terbutryn and terbuthylazine. The first-order and second-order kinetic models can be viewed in Eqs. (1) and (2), respectively:

$$DOC_t = DOC_i e^{-k_1 t} \quad (1)$$

$$\frac{1}{DOC_t} = \frac{1}{DOC_i} + k_2 t \quad (2)$$

Where k_1 and k_2 are the apparent kinetic rate constants of first- and second-order models, respectively. t is reaction time, DOC_i and DOC_t are the dissolved organic carbon concentrations in the beginning and at time t of the reaction.

The BMG kinetic model is shown in Eqs. (3) and (4) (also refers to Supplementary data, S1); Eq. (3) shows the rate of mineralisation (r_{DOC}) and Eq. (4) displays the final DOC concentration in the status of the reaction termination:

$$r_{DOC} = -\frac{dDOC_t}{dt} = DOC_i(1/m) \quad (3)$$

$$DOCt = DOC_i(1 - 1/b) \quad (4)$$

Where, DOC_i and DOC_t are dissolved organic carbon concentrations before the reaction and at the given reaction time t, respectively. *m* and *b* are the constants, which depict the initial mineralisation rate and the maximum oxidation capacity, respectively. $m < 1$ predicts the maximum amount of the compounds to be oxidised in the beginning of a given degradation reaction and $b > 1$ suggests the theoretical maximum oxidation of organics [46].

2.4. Analytical methods

Micropollutants concentration was estimated by Thermo Scientific Q- Exactive Orbitrap mass spectrometer with a positive electrospray ionisation mode. The samples were analysed against the calibration concentrations of 1.0–10^3 ng/mL by the given procedures as shown in Table 4.

DOC was measured by SHIMADZU TOC-L analyser. The Non-purgeable organic carbon method was used to calibrate and evaluate DOC concentration. 50 μL of samples were injected into the instrument to analyse DOC. The amount of dissolved Fe was analysed by AA400 Atomic Absorption Spectroscopy following the standard procedure.

2.5. Estimation of sludge production by sludge volume index (SVI)

The optimised dose of $FeSO_4$, Fe(0) and H_2O_2 were used for the estimation of sludge production. The mixture solution with five selected micro-pollutants (0.1 mg/L each) was prepared in distilled water to obtain a final concentration of 0.5 mg/L. To simulate the natural water conditions, the above stated solution was mixed with 0.5 mg/L humic acid solution to obtain a mixing ratio of 1:1 (w/w) of micro-pollutants: humic acid (MP_m: HA). The relevant Fenton reactions were run for 60 min and then allowed for sedimentation of 30 min. After that, the volume of sludge generated was read and recorded. Each experiment was replicated thrice to attain the reproducible results.

The mass of sludge was estimated by the amount of floc settled on filter paper after filtration. The 0.45 μm filter paper before and after filtration was dried in Panasonic Electric Oven (MOV-212 F) at 105° C for 10 min and 45 min, respectively, and left into desiccator to cool down to room temperature and then the paper or paper with sludge was weighted. The sludge mass was only recorded when the cooled down filtered paper attained a constant mass. Finally the sludge production or SVI value can be calculated using Eq. (5).

$$SVI\ \ (mL/g) = \frac{Setteled\ \ sludge\ \ volume\ \ (mL/L)}{Suspended\ \ solid\ \ concentration\ \ (mg/L)} \times 1000 \qquad (5)$$

2.6. Toxicity assessment

The Microtox acute toxicity protocol was employed for toxicity assay. BioFix Lumni freeze-dried Luminescent Bacteria (*Alivibrio fischeri*) was activated by adding 11 mL of Biofix Lumni medium into the stated bacteria. The solution was stored at 4°C for 30 min for stabilisation. The reference solution 18.7 mg/L Cr (VI) (52.9 mg/L potassium dichromate) was used as a positive control. Test samples were prepared using freeze-dried bacteria in 2% sodium chloride, providing an ambient condition for bacterial growth. The 0.1 mL bacterial solution was added into each fresh vial and incubated at 15°C for 15 min. Next, the initial Relative Light Unit (RLU) value (I_0) was measured. The control solutions and samples were added into the vials with already incubated bacteria. After 30 min incubation, RLU (I_{30}) was recorded. The correction ratio ($f_k = I_0/I_{30}$) for the individual control vials were calculated to find the mean correction value. The results obtained were evaluated as bioluminescence inhibition relative to the nagative control (2% NaCl solution, pollutants free). The test was considered valid if the individual values do not deviate from the mean by more than 5% ($\alpha = 0.05$). Triplicate of each sample were collected and analysed within a day to avoid misinterpretation data.

Table 4
LC/MS method and procedures.

LC/MS model	Thermo Scientific Q Exactive UHPLC equipped with electrospray ionisation interface (ESI)
Column and Polarity	Waters X select HSS column XP 2.5 μm. 2.1 × 150 mm; Positive
Eluent	A: 0.1% formic acid in methanol; B: 0.1% formic acid in Milli Q water
Run time and injection volume	0–17 min; 10 μL

2.7. Iron powder re-usability

Given volume of each micropollutant stock solution (1000 μg/L) was diluted together in tap water to form 500 mL of the mixed test solution with final concentration 100 μg/L. The experiment was induced with optimised initial pH and the molar ratio of H_2O_2:Fe powder. After each reaction, the solution was filtered to recover used Fe powder, which was washed with distilled water and dried in an oven (Panasonic Electric Oven (MOV-212 F)) at 100° C for 30 min and cooled at ambient temperature for reuse.

3. Results and discussion

3.1. Micro-pollutants removal

Fig. 1 shows overall performance of Fe(0) catalytic Fenton process to treat aqueous solution with each spiked micro-pollutants (10 μg/L). Though the reaction was optimised at initial pH 3, further experiments were conducted to check the feasibility of proposed Fe(0)- catalytic Fenton oxidation performance at pH 5. For pH 3, Fe(0) catalytic Fenton reaction was able to completely degrade each micro-pollutant (Fig. 1(a)) and can also mineralize the micropollutants mixture up to 70 ± 2.0% (Fig. 1(b)). Fig. 1(a) also shows that Fe(0) catalytic performance was less compromised at pH5 (except terbuthylazine). Pharmaceuticals like gabapentin are largely resistant to most treatment methods at pH5 [47, 48], while the Fe(0) catalytic Fenton process was able to degrade gabapentin up to 85.9 ± 6.1% at pH 5. The removals of sulfamethoxazole (antibiotic), diuron and terbutryn (pesticides) were around 98.4 ± 2.7%, 94.7 ± 4.5% and 100%, respectively. The removal of terbuthylazine was reduced at pH5, which was 69.2 ± 2.0%. The mixed micro-pollutants solution was mineralised by ~ 46 ± 1.0% for pH 5% and 70% for pH 3 (Fig. 1(b)).

This study also shows that complete degradation of the stated micro-pollutants was achieved at pH 3, irrespective of the type of catalyst used (Fig. S2.1). However, as shown in Table 5, the mineralisation of each micro-pollutant (i.e., DOC reduction) obtained in both treatments varied significantly; the Fe(0)-catalytic Fenton process showed greater DOC reduction than Fe(II)-catalytic Fenton process. Additionally, when each micropollutant was completely degraded, mineralisation of these compounds was assessed in order to determine the fate of micro-pollutants in the Fe(0)-Fenton oxidation; which is affected by the type of oxidation by-products formed as well as the compound starting concentration and other oxidation conditions. Example of this is that 96% mineralisation was achieved for diuron solution at 100 μg/L as compared to mineralisation of 85% and 69% for diuron solution at 10 μg/L and 1000 μg/L respectively. The possible reason of this could be that for the diuron concentration of 100 μg/L, the resulting oxidation products could have been less stable per the reaction conditions. This assumption however, needs further studies to verify.

Control experiments were carried out to validate the Fe(0) catalytic potential. Each micro-pollutant (100 μg/L) was treated by H_2O_2 alone at the pre-determined dose of 1.5–2.5 mM and the performance was compared with that of the Fe(0) catalytic Fenton reaction at the equivalent H_2O_2 doses; both was operated at pH 3 (Table 6). The results

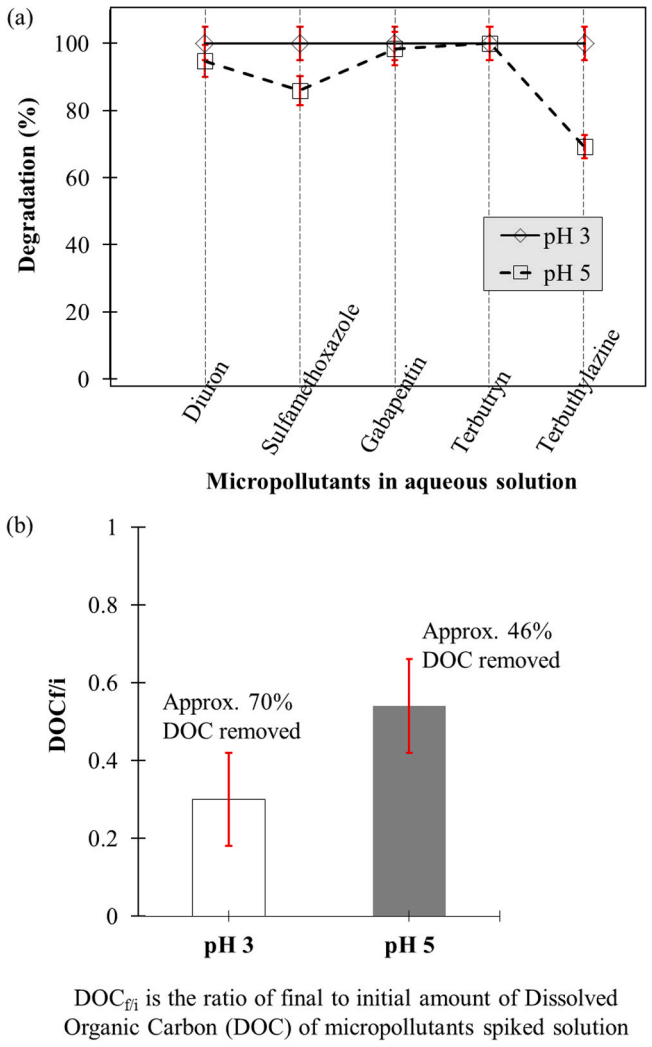

Fig. 1. (a) Fe(0) catalytic Fenton process performance in (a) degradation % of five micropollutants; (b) DOC removal ($DOC_{f/i}$ is the ratio of DOC concentrations of the test solutions before and after oxidation treatment).

Table 5
DOC removal from the spiked micro-pollutants test solutions by $FeSO_4$- and Fe (0)-Fenton catalytic oxidation process[a].

Substance	μg/L	DOC_i/DOC_0		DOC_i/DOC_0	
		$FeSO_4$	P-value	Fe (0)	P-value
Diuron	10	0.73	4.6×10^{-2}	0.15	3.0×10^{-3}
	100	0.23	4.1×10^{-4}	0.04	4.2×10^{-4}
	1000	0.43	5.9×10^{-5}	0.31	2.6×10^{-4}
Gabapentin	10	0.88	1.8×10^{-2}	0.69	7.6×10^{-4}
	100	1.06	0.28	0.32	6.4×10^{-3}
	1000	0.65	2.9×10^{-3}	0.29	2.4×10^{-3}
Sulfamethoxazole	10	0.86	0.14	0.45	0.04
	100	0.54	0.1	0.37	0.04
	1000	0.46	1.3×10^{-3}	0.16	1.3×10^{-3}
Terbutryn	10	0.60	9.4×10^{-3}	0.20	2.4×10^{-3}
	100	0.60	9.4×10^{-3}	0.16	1.2×10^{-3}
	1000	0.62	6.2×10^{-4}	0.12	3.2×10^{-4}
Terbuthylazine	10	0.02	1.1×10^{-3}	0.01	1.1×10^{-3}
	100	0.71	6.9×10^{-2}	0.56	0.03
	1000	0.74	1.1×10^{-2}	0.69	5.0×10^{-5}

The triplicate experiment results were validated from P-value evaluated from *t*-test.

[a] The data presented as a ratio of final to initial DOC concentration of the solution.

showed capability of H_2O_2 alone in the oxidation of the selected micropollutants; degradation efficiency ranged from 70% to 90%, while Fe(0) catalytic Fenton reaction achieved 100% degradation for all the micropollutants studied. Hence, H_2O_2 alone is ineffective to deliver similar results as it was used in the Fenton reaction.

3.2. Sludge production (as sludge volume index, SVI) and residual toxicity

The performance of Fe(0) catalytic- and $FeSO_4$ catalytic-Fenton processes was compared in terms of sludge production (as SVI) and residual toxicity. The flocs agglomeration or the sludge formation was observed after the $FeSO_4$ Fenton reaction and very tiny amount of Fe precipitates were observed when the test solutions pH slightly increased after 60 min Fenton reaction (Fig. S2.3). Fig. 2(a) compares the SVI values of both processes. Mean SVI value was 144.3 ± 5.4 for $FeSO_4$-catalytic Fenton process and 25.5 ± 1.9 for Fe(0)-catalytic Fenton process, respectively. Significant reduction of sludge production from Fe(0)-catalytic Fenton process could attribute to the existence very low level of soluble iron species in the solution which is to be discussed further in Section 3.5.

As shown in Fig. 2(b) (also refers to Fig. S2.2), initial samples (multiple pollutants' mixture (M^P_m)) were toxic (increasing bioluminescence inhibition). On the other hand, most treated effluents by each process were non-toxic except $FeSO_4$-final-2 sample, which showed possible toxicity with ± 15.1 deviations. This study confirmed the previous results [49] where Fe(0)-catalytic Fenton reaction completely removed the toxicity caused by organic micropollutants. High toxicity removal from Fenton treatment can be inferred with the formation of oxidation by-products with low molecular mass and short chain, which could exhibit non- or low-toxicity. This has been observed as well in the micropollutants' degradation by ferrate oxidation, where short-chain oxidation by-products were generated and exhibited lower and no toxicity al all [50,51]. Additionally, oxidant used in the Fenton reaction is H_2O_2 which can break down to form non-toxic compounds like H_2O and O_2 and then contributes no toxicity at all in the reactions.

3.3. Synergistic reactivity of Fe(0) powder in the Fenton reaction

The advantage of Fe(0) catalytic Fenton process over the traditional Fe(II)-Fenton process was found as a result of the co-occurrence of the oxidation reaction in conjunction with the interface sorption. Fig. 3 proposes the mechanism investigated to comprehend the mentioned synergistic reactivity. Broadly, the reactions occurring during the process can be summarised as 1) Fe(0) surface activation under acidic environment, 2) degradation of micro-pollutants by oxidation and 3) sorption of organics on the surface of activated Fe(0) powders.

Several pathways of Fe(0)-Fenton process shown in Fig. 3 is driven by the corrosion of Fe(0) powders. As suggested in [52], the levels of Fe (0) surface activation was found significant in determining the heterogeneous Fenton process' reactivity. Surface area of the fresh Fe(0) powder was 952 μm^2 (Area thresholding method, Table S2.1) which promoted mass transfer in terms of both the catalysis and surface sorption after its activation, and results in higher DOC removal in comparison to the $FeSO_4$-catalytic Fenton oxidation, as discussed above.

In aqueous solution under aerobic condition, Fe(0) is corroded by O_2, and here, the effect was accelerated in an acidic environment to promote to generate more ferrous ions (Eq. 6).

$$2\,Fe(0) + O_2 + 4\,H^+ \rightarrow 2\,Fe^{2+} + H_2O \quad (6)$$

The reactions displayed in Eq. (6) show two moles of Fe(0) are oxidised by one mole of O_2 to form two moles of Fe(II) ions, which involved in four-electrons' transfer. The Fe(0) surface oxidation consumed H^+ ions and then, in contrast to the traditional Fenton process, the pH of the solution was slightly increased during the Fe(0) catalytic Fenton process

Table 6
Comparative degradation by H_2O_2 alone and Fe(0) catalytic Fenton reaction.

Process	Diuron	Gabapentin	Sulfamethoxazole	Terbutryn	Terbuthylazine
	Degradation efficiency (%)				
H_2O_2 alone	90	76	90	85	70
Fe(0) catalytic Fenton reaction	100	100	100	100	100

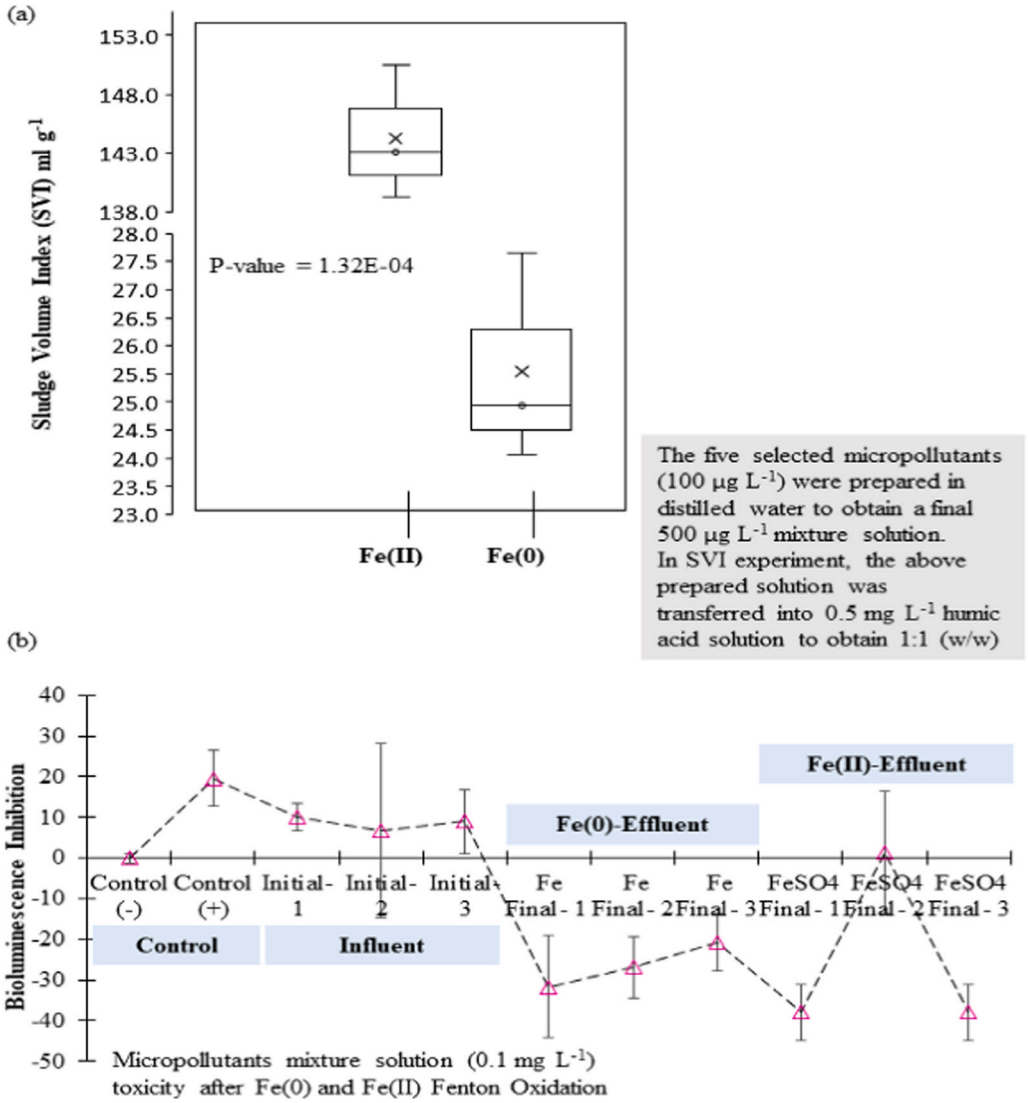

Fig. 2. (a) Sludge volume index (mL/g) from Fe(0)- and $FeSO_4$-catalytic Fenton processes; (b) Microtox toxicity assay for solution samples of untreated and after treatment by $FeSO_4$ and Fe (0) Fenton oxidation.

(Fig. S2.3). Hence, the pH reduction complications in the Fe(II) catalytic Fenton process can be resolved. This, together with the significant reduction of sludge production (as shown previously), suggests that the Fe(0)-catalytic heterogeneous Fenton process could be used to replace the classical homogeneous Fenton oxidation for a large-scale water purification in practice.

Rather than sole oxidation process, the Fe(0) catalytic Fenton process has numerous reaction schemes, and the prominent sorption occurred after Fe(0) surface's activation, and this was evidenced by the Fourier Transform Infrared (FTIR) analysis of the oxidised Fe(0) powder surface. The Infrared (IR) spectrum in BioRad illustrates low molecular weight organic compounds found on the corroded Fe powder surface after the Fenton reaction (Figs. S2.4–2.8). Based on the functional groups presented, the adsorbed organics are mainly the oxidation by-products formed in the Fe(0)-Fenton degradation process, as shown in Fig. 4. A separate experiment was conducted where a 100 µg/L gabapentin solution (pH 3) was mixed with given iron powder only (no oxidant addition) and left for overnight. The result showed 91.2 ± 6.8% of gabapentin was removed, which suggests the sorption potentials of micro-pollutant to the Fe(0) powder's surface and provides evidence of synchronisation of oxidation and sorption effect in Fe(0) catalytic-Fenton process.

3.4. Assessment of kinetic rate constant

The kinetic rate of micro-pollutants' mineralisation was evaluated using the First and Second order models and the BMG-model (Fig. S2.9), and the rate constants and the regression coefficient for each model are

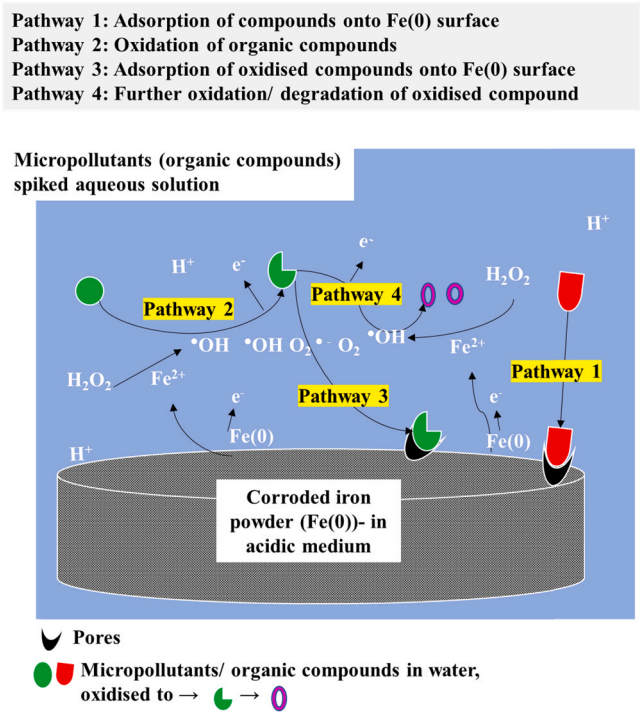

Fig. 3. Pathways causing micro-pollutants removal during Fe(0) catalytic Fenton reactions - synchronisation of redox reactions and surface adsorption.

given in Table 7. The BMG model possesses high linearity and thus can well represent the mineralisation rate of Fe(0)-catalytic Fenton process. It can be viewed from Table 4 that terbuthylazine had relatively slower kinetic mineralisation rate in comparison with the rates of other pollutants. This is consistent to the DOC removal results shown in Table 5, where DOC of terbuthylazine was less removed, especially when starting DOC was 100 and 1000 µg/L.

3.5. Re-usability of Fe powders for the Fenton reaction

Preliminary tests showed that Fe powders can be proficiently reused up to three times in terms of the constant reduction efficiency of micropollutants (Fig. 5). The DOC reduction was compromised to around 20% at third cycle of reusing Fe powder (Fig. 5a). Additionally, after the Fenton reactions, the iron powder was recovered and treated, more than 94% of them can be recovered after each application, with a relatively low amount of dissolved Fe ions in the solutions, leading to no (when pH 3 – 3.5) or less (for pH 5 – 5.5) sludge formed, respectively. This suggests a high efficiency of recovery and reuse of Fe powders for the catalyst functions in the Fenton reaction (Fig. S2.10). Scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDXRS) measurements (Fig. S2.11) show the decreasing in Fe content and increasing in oxygen content after Fenton reactions (Table 8), suggesting the formation of iron oxide layers on the Fe-powder surface, which reduced the capacity of both catalysis and sorption functions of Fe powders [53]; and

Table 7
Fe(0) Fenton oxidation kinetic rate constants.

	First order model		Second order model		BMG kinetic model	
	$k \times 10^{-2}$ (1/min)	R^2	$k \times 10^{-2}$ (1/(M min))	R^2	-k (1/mg/(L min))	R^2
Diuron	0.29	0.84	1.41	0.89	0.36	1
Gabapentin	0.17	0.96	0.66	0.96	0.35	1
Sulfamethoxazole	0.24	0.94	0.92	0.95	0.39	1
Terbutryn	0.24	0.95	1.08	0.92	0.44	1
Terbuthylazine	0.1	0.82	0.36	0.82	0.31	1

k: Mineralisation kinetic rate constant; R^2: Regression coefficient.

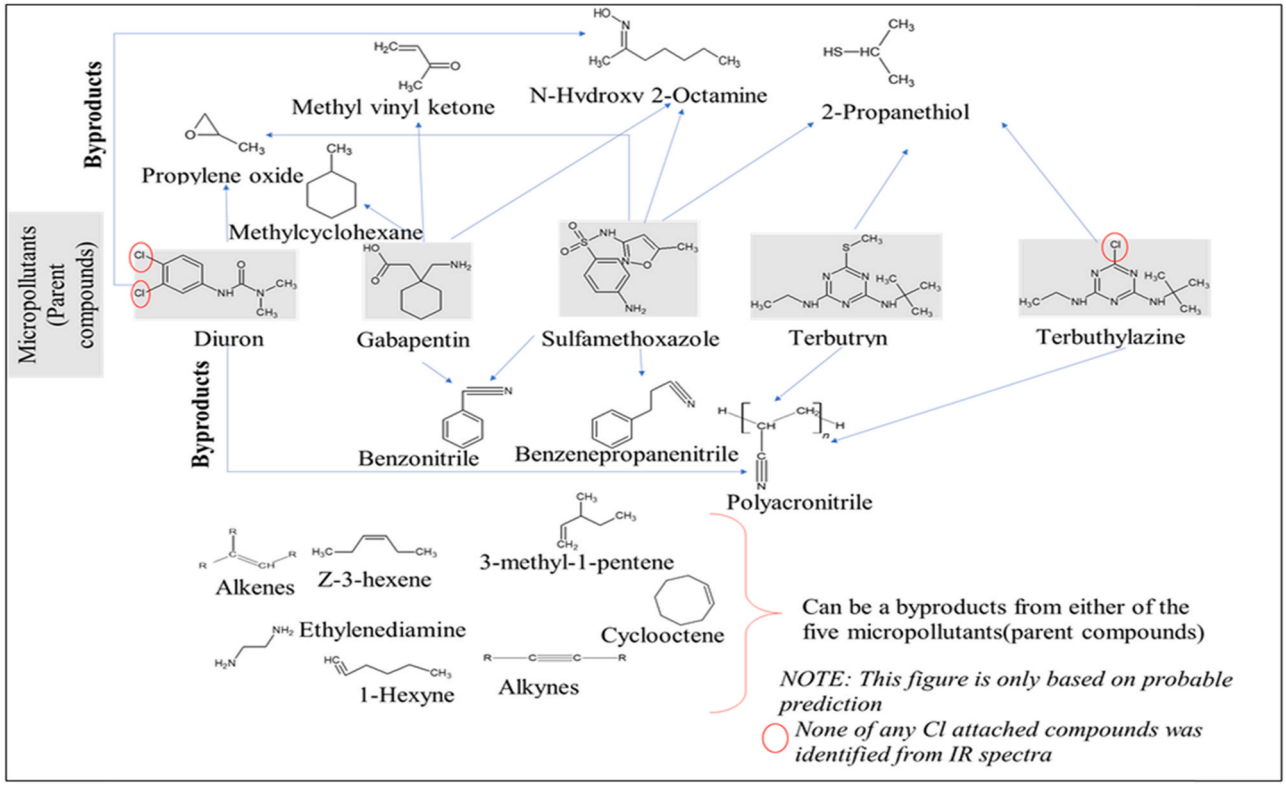

Fig. 4. Oxidation by-products found on the Fe(0) powder surface after the Fenton reaction.

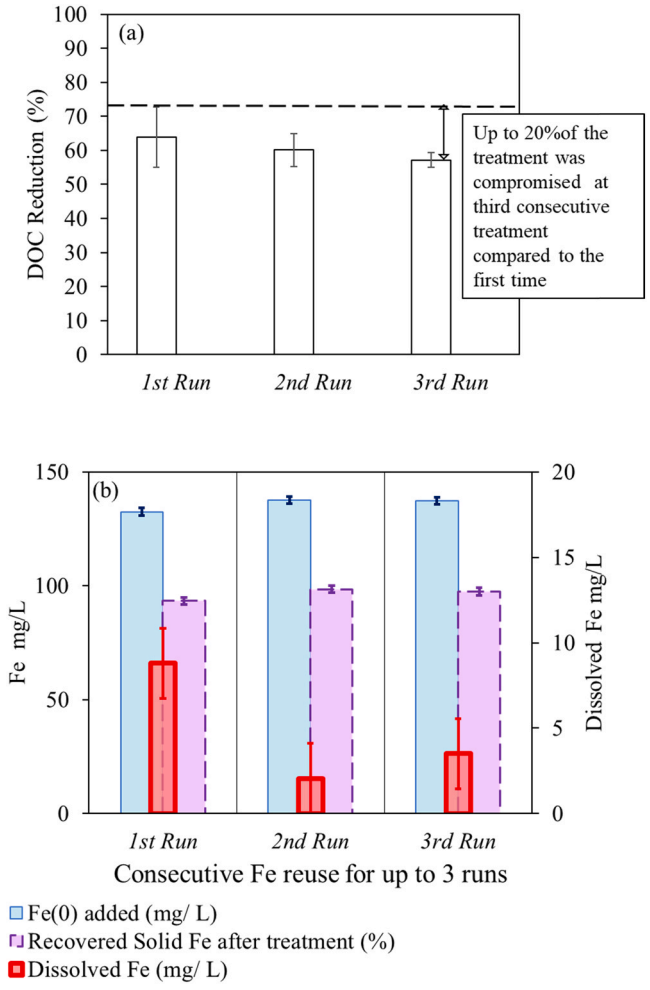

Fig. 5. Fe powder reusability in the Fe(0)-Fenton reaction: (a) DOC reduction performance in three consecutive runs; (b) Fe powder recovered after each run for up to three times.

this could explain decreasing in the degradation efficiency after the third run of Fe(0) catalytic Fenton reaction.

4. Conclusions and future work recommendation

Using Fe(0) catalytic Fenton process, we found that 100% reduction of five studied micropollutants was achieved at pH 3 though the reduction efficiency was slightly reduced by 5–15% at pH 5 (except terbuthylazine); DOC in multiple micropollutant solutions can be reduced by 70% at pH 3 and 46% at pH 5, which were much better than the Fe(II)-catalytic Fenton reaction for the same pH conditions. The results showed that when Fe(0) powders initiated the catalytic Fenton reaction, simultaneous adsorption of the studied micropollutants occurred, which explains the relatively better performance of Fe(0) catalytic Fenton reaction in comparison with that of the Fe(SO_4)–catalytic Fenton reaction. Additionally, Fe(0) powder could be reusable up to three times although the DOC reduction was decreased by 20% at the third run. And, studies showed that the BMG model fitted well to the kinetics of degrading the studied micropollutants in the Fe(0) catalytic Fenton reactions. Although the traditional Fenton oxidation can highly degrade a lot of organic pollutants, the primary drawback of the process is heavy sludge production caused by the consumption of catalyst and low pH requirements. The current work suggests that the Fe(0)-catalytic Fenton oxidation can not only achieve high degradation of the selected micropollutants at pH up to 5, but also produced no or much less sludge, reduced the toxicity and demonstrated Fe(0) powder reusable potentials. And thus, Fe(0) catalytic Fenton process is an alternative to the traditional Fenton process to combat the negative issues caused by emerging micropollutants. Full economic assessment, though, needs fully assessed before the process can be used in large scale environmental remediation. Moreover, more fundamental studies are needed to investigate the efficiency of radicals generation, passivation minimisation on the Fe(0) powder surface and increasing the degradation efficiency when water pH was greater than 5; all these will reach the technology more applicable in practice.

Table 8
Element composition of Fe and O on the surface of raw and reacted Fe(0) powders.

	Reaction Time (min)	Fe (%)	O (%)	Reference
Raw Fe(0) powder	0	100	0	This study
10 μg/L M^P_m	60	59.9	39.4	This study
100 μg/L M^P_m	60	58.5	40.5	This study
1000 μg/L M^P_m	60	64.9	34.3	This study
Raw Fe(0) powder	0	90.3	9.7	[53]
4-chlorophenol	30	51.02	48.98	[53]

M^P_m: Mixtures of equal contents of diuron, gabapentin, sulfamethoxazole, terbutryn and terbuthylazine in water.

CRediT authorship contribution statement

Anuradha Goswami: Conceptualization, Methodology, Investigation, Validation, Writing - draft. **Jia-Qian Jiang:** Conceptualization, Methodology, Investigation, Validation, Supervision, Funding acquisition, Project administration, Writing - review, editing, finalising and provided extensive contributions to the preparation of the final version of the manuscript. **Michael Petri:** Conceptualization, Resources, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare no conflict of interest that could influence the work reported and submission of this manuscript.

Acknowledgements

The authors are grateful to Glasgow Caledonian University (GCU, UK) for offering the research studentship to A. Goswami for the PhD study. We also appreciate additional research financial support from Lake Constance Water Supply of Germany and technicians' support at GCU for LC/MS analysis. The views of this paper do not necessarily represent that of the companies.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2021.105393.

References

[1] B. Kasprzyk-Hordern, R.M. Dinsdale, A.J. Guwy, The occurrence of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs in surface water in South Wales, UK, Water Res. 42 (2008) 3498–3518, https://doi.org/10.1016/j.watres.2008.04.026.
[2] J.-Q. Jiang, Z. Zhou, V.K. Sharma, Occurrence, transportation, monitoring and treatment of emerging micro-pollutants in waste water - a review from global views, Microchem. J. 110 (2013) 292–300, https://doi.org/10.1016/j.microc.2013.04.014.
[3] A.R. Ribeiro, O.C. Nunes, M.F.R. Pereira, A.M.T. Silva, An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU, Environ. Int. 75 (2015) 33–51, https://doi.org/10.1016/j.envint.2014.10.027.
[4] S.D. Richardson, S.Y. Kimura, Water analysis: emerging contaminants and current issues, Anal. Chem. 92 (2020) 473–505.
[5] P.W. Seo, B.N. Bhadra, I. Ahmed, N.A. Khan, S.H. Jhung, Adsorptive removal of pharmaceuticals and personal care products from water with functionalized metal-

organic frameworks: remarkable adsorbents with hydrogen-bonding abilities, Sci. Rep. 6 (2016) 34462, https://doi.org/10.1038/srep34462.
[6] S. Suárez, M. Carballa, F. Omil, J.M. Lema, How are pharmaceutical and personal care products (PPCPs) removed from urban wastewaters? Rev. Environ. Sci. Biotechnol. 7 (2008) 125–138.
[7] B. Kasprzyk-Hordern, R.M. Dinsdale, A.J. Guwy, The occurrence of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs in surface water in South Wales, UK, Water Res. 42 (2008) 3498–3518.
[8] M.P. Ormad, N. Miguel, M. Lanao, R. Mosteo, J.L. Ovelleiro, Effect of application of ozone and ozone combined with hydrogen peroxide and titanium dioxide in the removal of pesticides from water, Ozone Sci. Eng. 32 (2010) 25–32, https://doi.org/10.1080/01919510903482764.
[9] M. Hladik, D.L. Calhoun, Analysis of the herbicide diuron, three diuron degradates, and six neonicotinoid insecticides in water — method details and application to two georgia streams, USGS Sci. Investig. Rep. 2012- 5206 (2012) 10.
[10] L.C. Cabrera, S.S. Caldas, S. Rodrigues, A. Bianchini, F.A. Duarte, E.G. Primel, Degradation of herbicide diuron in water employing the Fe 0/H2O2 system, J. Braz. Chem. Soc. 21 (2010) 2347–2352, https://doi.org/10.1590/S0103-50532010001200023.
[11] C. Hartles, M. Janson, F. Jenkins, J. Lin, A. Ullagaddi, Risks of 2, 4-D Use to the Federally Threatened California Red-legged Frog (Rana aurora draytonii) and Alameda Whipsnake Office of Pesticide Programs, Washington, D.C., 2009. https://www3.epa.gov/pesticides/endanger/litstatus/effects/redleg-frog/2-4-d/analysis.pdf.
[12] Pregabalin and gabapentin to be controlled as class C drugs, Open Gov. Licence v3.0., 2018. https://www.gov.uk/government/news/pregabalin-and-gabapentin-to-be-controlled-as-class-c-drugs.
[13] A.L. Srinivasan, P., Sarmah, A.K., Manley-Harris, M. & Wilkins, Sorption of sulfamethoxazole, sulfachloropyridazine and sulfamethazine onto six New Zealand dairy farm soils, 19th World Congr. Soil Sci. Soil Solut. a Chang. World, 2010.
[14] IACR, IACR Monographs Volume 79: Sulfomethoxazole, 79, 1979.
[15] P.M. Álvarez, D.H. Quiñones, I. Terrones, A. Rey, F.J. Beltrán, Insights into the removal of terbuthylazine from aqueous solution by several treatment methods, Water Res. 98 (2016) 334–343, https://doi.org/10.1016/j.watres.2016.04.026.
[16] European Commission, Priority substances under the Water Framework Directive, Eur. Comm. Website., 2016. https://ec.europa.eu/environment/water/water-dangersub/pri_substances.htm (Accessed 15 February 2021).
[17] D.J. Lapworth, D. Gooddy, I. Harrison, J. Hookey, Pesticides and their metabolites in groundwater: diuron in the Isle of Thanet aquifer of southeast England, Groundw. Syst. Qual. (2005). http://nora.nerc.ac.uk/4491/.
[18] J. Ra, H. Yoom, H. Son, Y. Lee, Occurrence and transformation of gabapentin in urban water quality engineering: rapid formation of nitrile from amine during drinking water chlorination, Water Res. 184 (2020), 116123. https://doi.org/10.1016/j.watres.2020.116123.
[19] R. Gurke, M. Rößler, C. Marx, S. Diamond, S. Schubert, R. Oertel, J. Fauler, Occurrence and removal of frequently prescribed pharmaceuticals and corresponding metabolites in wastewater of a sewage treatment plant, Sci. Total Environ. 532 (2015) 762–770, https://doi.org/10.1016/j.scitotenv.2015.06.067.
[20] I. Rosendahl, C. Nguyen Dang Giang, W. Amelung, Q. Hoang Minh, Z. Sebesvari, F. Renaud, Occurrence and dissipation of the antibiotics sulfamethoxazole, sulfadiazine, trimethoprim, and enrofloxacin in the Mekong Delta, Vietnam, PLoS One 10 (2015), e0131855, https://doi.org/10.1371/journal.pone.0131855.
[21] K. Quednow, W. Püttmann, Monitoring terbutryn pollution in small rivers of Hesse, Germany, J. Environ. Monit. 9 (2007) 1337–1343, https://doi.org/10.1039/b711854f.
[22] A. Barra Caracciolo, C. Fajardo, P. Grenni, M.L. Saccà, S. Amalfitano, R. Ciccoli, M. Martin, A. Gibello, The role of a groundwater bacterial community in the degradation of the herbicide terbuthylazine, FEMS Microbiol. Ecol. 71 (2010) 127–136, https://doi.org/10.1111/j.1574-6941.2009.00787.x.
[23] A. Goswami, J.-Q. Jiang, M. Petri, Non-parametric regression analysis of diuron and gabapentin degradation in lake constance water by ozonation and their toxicity assessment, Water 11 (2019) 852, https://doi.org/10.3390/w11040852.
[24] D. Ma, J. Wei, H. Zhang, Y. Zhou, J. Shen, L. Wang, P. Zhang, Acute toxicity evolution during ozonation of mono-chlorophenols and initial identification of highly toxic intermediates, Environ. Sci. Process. Impacts 21 (2019) 1509–1518, https://doi.org/10.1039/c9em00225a.
[25] M. Trapido, T. Tenno, A. Goi, N. Dulova, E. Kattel, D. Klauson, K. Klein, T. Tenno, M. Viisimaa, Bio-recalcitrant pollutants removal from wastewater with combination of the Fenton treatment and biological oxidation, J. Water Process Eng. 16 (2017) 277–282, https://doi.org/10.1016/j.jwpe.2017.02.007.
[26] K.-D. Zoh, M.K. Stenstrom, Fenton oxidation of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), Water Res. 36 (2002) 1331–1341, https://doi.org/10.1016/S0043-1354(01)00285-8.
[27] M.M. Ballesteros Martín, J.L. Casas López, I. Oller, S. Malato, J.A. Sánchez Pérez, A comparative study of different tests for biodegradability enhancement determination during AOP treatment of recalcitrant toxic aqueous solutions, Ecotoxicol. Environ. Saf. 73 (2010) 1189–1195, https://doi.org/10.1016/j.ecoenv.2010.07.021.
[28] R.C. Martins, M. Gmurek, A.F. Rossi, V. Corceiro, R. Costa, M.E. Quinta-Ferreira, S. Ledakowicz, R.M. Quinta-Ferreira, Application of Fenton oxidation to reduce the toxicity of mixed parabens, Water Sci. Technol. 74 (2016) 1867–1875, https://doi.org/10.2166/wst.2016.374.
[29] D.H. Quinones, A. Rey, P.M. Alvarez, F.J. Beltran, G. Li Puma, Boron doped TiO2 catalysts for photocatalytic ozonation of aqueous mixtures of common pesticides: diuron, o-phenylphenol, MCPA and terbuthylazine, Appl. Catal. B Environ. 178 (2014) 74–81, https://doi.org/10.1016/j.apcatb.2014.10.036.
[30] S. Besnault, S.M. Ruel, S. Baig, M. Esperanza, H. Budzinski, C. Miege, C. Boucher, K. Le Menach, M. Coquery, Technical, economic and environmental evaluation of advanced tertiary treatments for micropollutants removal (oxidation and adsorption), 2014.
[31] H. Katsumata, M. Sada, Y. Nakaoka, S. Kaneco, T. Suzuki, K. Ohta, Photocatalytic degradation of diuron in aqueous solution by platinized TiO2, J. Hazard. Mater. 171 (2009) 1081–1087, https://doi.org/10.1016/j.jhazmat.2009.06.110.
[32] S. Teixeira, R. Gurke, H. Eckert, K. Kühn, J. Fauler, G. Cuniberti, Photocatalytic degradation of pharmaceuticals present in conventional treated wastewater by nanoparticle suspensions, J. Environ. Chem. Eng. 4 (2016) 287–292, https://doi.org/10.1016/j.jece.2015.10.045.
[33] W.-Q. Guo, R.-L. Yin, X.-J. Zhou, H.-O. Cao, J.-S. Chang, N.-Q. Ren, Ultrasonic-assisted ozone oxidation process for sulfamethoxazole removal: impact factors and degradation process, Desalin. Water Treat. 3994 (2015) 1–8, https://doi.org/10.1080/19443994.2015.1115373.
[34] L. Muszkat, M. Halmann, D. Raucher, L. Bir, Solar photodegradation of xenobiotic contaminants in polluted well water, J. Photochem. Photobiol. A Chem. 65 (1992) 409–417, https://doi.org/10.1016/1010-6030(92)80022-N.
[35] N. De la Cruz, J. Giménez, S. Esplugas, D. Grandjean, L.F. De Alencastro, C. Pulgarín, Degradation of 32 emergent contaminants by UV and neutral photo-fenton in domestic wastewater effluent previously treated by activated sludge, Water Res. 46 (2012) 1947–1957, https://doi.org/10.1016/j.watres.2012.01.014.
[36] P. Wardman, L. Candeias, Fenton chemistry: an introduction, Radiat. Res. 145 (1996) 523–531.
[37] A. Goswami, J.-Q. Jiang, Comparative performance of catalytic fenton oxidation with zero-valent iron (Fe(0)) in comparison with ferrous sulphate for the removal of micropollutants, Appl. Sci. 9 (2019) 2181, https://doi.org/10.3390/app9112181.
[38] S. Huo, D. Necas, F. Zhu, D. Chen, J. An, N. Zhou, W. Liu, L. Wang, Y. Cheng, Y. Liu, R. Ruan, Anaerobic digestion wastewater decolorization by H2O2-enhanced electro-Fenton coagulation following nutrients recovery via acid tolerant and protein-rich Chlorella production, Chem. Eng. J. 406 (2021), 127160, https://doi.org/10.1016/j.cej.2020.127160.
[39] Y.W. Kang, K.-Y. Hwang, Effects of reaction conditions on the oxidation efficiency in the Fenton process, Water Res. 34 (2000) 2786–2790, https://doi.org/10.1016/S0043-1354(99)00388-7.
[40] J. Poerschmann, U. Trommler, T. Górecki, Aromatic intermediate formation during oxidative degradation of Bisphenol A by homogeneous sub-stoichiometric Fenton reaction, Chemosphere 79 (2010) 975–986, https://doi.org/10.1016/j.chemosphere.2010.03.030.
[41] M. Tyagi, N. Kumari, S. Jagadevan, A holistic Fenton oxidation-biodegradation system for treatment of phenol from coke oven wastewater: optimization, toxicity analysis and phylogenetic analysis, J. Water Process Eng. 37 (2020), 101475, https://doi.org/10.1016/j.jwpe.2020.101475.
[42] C.C. Winterbourn, Toxicity of iron and hydrogen peroxide: the Fenton reaction, Toxicol. Lett. 82–83 (1995) 969–974, https://doi.org/10.1016/0378-4274(95)03532-X.
[43] N. Wang, T. Zheng, G. Zhang, P. Wang, A review on Fenton-like processes for organic wastewater treatment, J. Environ. Chem. Eng. 4 (2016) 762–787, https://doi.org/10.1016/j.jece.2015.12.016.
[44] B.D. Hasan, A.A.A. Raman, W.M.A.W. Daud, On the limitation of fenton oxidation operational parameters: a review, Int. J. Chem. React. Eng. 10 (2012), https://doi.org/10.1515/1542-6580.2913.
[45] The Drinking Water Quality Regulator for Scotland, 2019. "Scotland's Water Quality Compliance" Drinking Water Quality regulators for Scotland (DWQR) [WWW Document]. © Crown Copyr. 2018. https://dwqr.scot/public-water-supply/national-water-quality/scotlands-water-quality-compliance/ (Accessed 15 November 2019).
[46] M.A. Behnajady, N. Modirshahla, F. Ghanbary, A kinetic model for the decolorisation of C.I. Acid Yellow 23 by Fenton process, J. Hazard. Mater. 148 (2016) 98–102, https://doi.org/10.1016/j.jhazmat.2007.02.003.
[47] M. Herrmann, J. Menz, O. Olsson, K. Kümmerer, Identification of phototransformation products of the antiepileptic drug gabapentin: biodegradability and initial assessment of toxicity, Water Res. 85 (2015) 11–21, https://doi.org/10.1016/j.watres.2015.08.004.
[48] F. Li, J. Bao, T.C. Zhang, Y. Lei, A combined process of adsorption and Fenton-like oxidation for furfural removal using zero-valent iron residue, Environ. Technol. 36 (2015) 3103–3111, https://doi.org/10.1080/09593330.2015.1054317.
[49] E. GilPavas, S. Correa-Sánchez, D.A. Acosta, Using scrap zero valent iron to replace dissolved iron in the Fenton process for textile wastewater treatment: optimisation and assessment of toxicity and biodegradability, Environ. Pollut. 252 (2019) 1709–1718, https://doi.org/10.1016/j.envpol.2019.06.104.
[50] S. Zhang, J.-Q. Jiang, Comparative removal of imidacloprid, bisphenol-S, and azithromycin with ferrate and FeCl3 and assessment of the resulting toxicity, J. Chem. Technol. Biotech. 96 (2021) 99–112, https://doi.org/10.1002/jctb.6515.
[51] S. Zhang, J.-Q. Jiang, M. Petri, Preliminarily comparative performance of removing bisphenol-S by ferrate oxidation and ozonation, npj Clean. Water 4 (1) (2021) 1, https://doi.org/10.1038/s41545-020-00095-x.
[52] F.W. Billmeyer Jr., Textbook of Polymer Science, third ed., John Wiley & Sons,, New York, 1984.
[53] T. Zhou, Y. Li, J. Ji, F.-S. Wong, X. Lu, Oxidation of 4-chlorophenol in a heterogeneous zero valent iron/H_2O_2 Fenton-like system: kinetic, pathway and effect factors, Sep. Purif. Technol. 62 (2008) 551–558, https://doi.org/10.1016/j.seppur.2008.03.008.